Device for sample preparation

The invention relates to a method for preparation of a sample, in particular for extraction and enrichment of a volatile component from a liquid, solid or gaseous sample for subsequent introduction into an analytical device, for example a gas chromatograph. A device for carrying out this method comprises a syringe, and a hollow needle connected to the syringe body.

To allow components of interest from a sample, for example volatile impurities from an environmental sample, to be analyzed in a gas chromatograph, the sample has to be prepared in such a way that the components of interest are extracted from the sample and enriched. DE 19525771 discloses a solid-phase extraction which uses a syringe to transfer the components of interest into a chromatograph, the needle of said syringe being provided with a coating of a stationary phase. By suctioning a sample into the needle, if appropriate several times, an extraction of components of interest takes place. The components detached by desorption from the stationary phase are then introduced into the injection inlet of a gas chromatograph. The syringe can be operated manually or automatically.

A similar device with a syringe whose needle is coated with a stationary phase is known from WO99/31480. In this device, a delivery system is additionally provided for a carrier gas which is inert in relation to the analyte and by means of which the components of interest are desorbed and delivered to a gas chromatograph. DE10024443 likewise describes a device with a syringe whose needle has a coating of a stationary phase on which the analyte of interest adsorbs and is then introduced by desorption into a gas

chromatograph. For this purpose, the needle is flushed with a carrier fluid during the desorption phase.

These known systems have the disadvantage that, because of the limited surface (a few mm^2) of the extraction material, the extraction, i.e. the uptake of the components of interest, is slow and incomplete. For this reason, the efficiency of these known systems is not optimal. Therefore, the object of the invention is to remedy this disadvantage.

According to the invention, this is achieved by a method of the type mentioned at the outset, which is characterized in that the sample is flushed through an extraction material for extraction of the analytes of interest. A device for carrying out this method is characterized in that, between the needle and the syringe body, a chamber is provided which is wider than the cross section of the needle and in which an extraction material is located.

According to a preferred embodiment of the invention, the extraction material comprises particles or beads coated with stationary phase (e.g. Chromosorb coated with Carbowax 20M). According to another preferred embodiment, the extraction material comprises absorption materials such as are used in chromatography (e.g. Carbosieve S3, Carbopack, Tenax, activated charcoal, etc.).

Preferred illustrative embodiments of the invention are described below with reference to the attached drawings, in which:

Fig. 1 shows a cross section through an embodiment of the device according to the invention,

Figs 2-5 show schematic representations of different method sequences.

As is shown in Fig. 1, a gastight syringe 1 comprises a syringe body 2, and a plunger 3 which is axially movable in the latter. At its lower end, the syringe body has, as usual, an outlet opening 6 with a connector 7, which is configured as a Luer connector for example. An extraction tube 9 is connected to the connector 7 by means of an attachment piece 8. Arranged at the lower end of the extraction tube is the hollow needle 10 which, in standard syringes, would be fitted onto the Luer connector 7.

Alternatively, it is possible for the extraction tube and the hollow needle to be produced in one piece.

The extraction tube 9 has a diameter of between 0.5 and 4 mm and a length of 2 to 60 mm. In its interior, a packing 12 is located between two hoops 11. The hoops are made of sintered metal beads. Alternatively, other materials can also be used for the hoops, for example tufts of glass wool, metal screens, etc.

For the purpose of this description, the term extraction material is to be understood as meaning that at least part of the interior of the extraction tube 9 between the hoops 11 is filled in the manner of a packing with the material. As extraction material, particles are used which are of the kind used as absorbents or as packing materials in gas chromatography, for example Tenax, Chromosorb, Carbopack, activated charcoal, etc. All the materials used, whether organic or inorganic, have the common property that molecules are adsorbed on their surface and are thus able to accumulate.

The extraction tube 9 is provided with a heating jacket 13. The heating permits thermal desorption. Instead of the heating jacket, radiant heating or direct heating

of the tube with low voltage and relatively high current strength is possible.

The typical procedure with the device described here is as follows: The sample 16 to be analyzed is generally located in a gastight sample vial 14. Some of the gas located in the space 15 above the sample (the head space) is sucked through the extraction material with the aid of the syringe, whereby the molecules to be analyzed (analyte) are absorbed on the surface and accumulate there after a quantity of gas has been drawn in several times. In a further step, these molecules are fed to an analytical device (e.g. a gas chromatograph), either by the extraction tube being heated and having gas passed through it (thermal desorption), or the analyte being washed from the particles by a solvent and being delivered with the solvent to the analytical device (liquid desorption).

The method is carried out using a liquid sample, specifically in the manner shown in Figures 2 to 4, as follows:

First, the sample is prepared or worked up by means of the molecules to be analyzed, i.e. the analyte, being separated from the liquid. There are three preferred possible ways of doing this:

Either, as is shown in Fig. 2, the syringe needle is introduced into the gas space of the sample vial. By repeated intake and ejection of the gas with the syringe, the substances to be analyzed are transferred at least partially to the extraction material.

Or, as shown in Figures 3a and 3b, the tip of the syringe needle is first introduced into the gas space 15 of the sample vial 14 and some of the gas is drawn into the syringe using the syringe. The needle tip is then immersed in the liquid 16 and the gas expelled,

whereupon volatile molecules are blown from the liquid into the gas space. Thereafter, the needle tip is then drawn back again into the gas space and some of the gas is drawn into the syringe through the extraction material. This procedure can be repeated in order to increase the efficiency of the extraction.

As a third alternative, the liquid can be drawn directly through the extraction material into the syringe. This procedure too can be repeated in order to heighten the efficiency.

The first of the three described procedures is used to work up a solid sample.

To avoid contamination of the system by ambient air, the syringe can be partly filled with clean gas before being introduced into the sample vial.

To transfer the substances into the analytical device, thermal desorption or liquid desorption is used. Thermal desorption is based on the fact that the substances deposited on the particles detach again from the particles at elevated temperatures and convert to the gaseous phase. If the extraction material is heated and gas is conveyed through it, the substances to be analyzed can be transferred in this gaseous stream into the analytical device. In liquid desorption, the substances are detached from the particles with a solvent and transferred to the analytical device.

For thermal desorption, there are once again several possibilities, in each case with simultaneous heating of the packing. It can either be carried out, as is shown in Fig. 4, by delivering a clean gas through a gas inlet 17 arranged between the syringe and the packing. This procedure is the most elegant, but also the most complicated way of bringing the substances from the filter into the gas chromatograph. Since the

syringe plunger is pressed fully down and the lateral gas admission line has only a very small volume during the injection, the danger of gas flowing in the wrong direction is negligible. The desorption gas pressure must be slightly higher than the gas pressure in the injector. In this procedure, the substances are moreover transferred gently into the analytical device, because only gas that is free of oxygen can be used. However, the procedure requires an additional valve and a pressure control means, i.e. a certain level of expenditure in terms of equipment.

Alternatively, as is shown in Fig. 5, it can be carried out using gas from the sample vial. This procedure is technically the simplest, since no additional gas valves or appliances are required. However, it has the disadvantage that the substances to be analyzed are exposed to higher temperatures and oxygen during the desorption, which can lead to oxidation of the substances. This procedure is suitable, however, for analyzing chemically stable compounds such as hydrocarbons or chlorinated solvents.

Finally, it can be carried out with high-purity gas from a gas reservoir. The gas reservoir is generally a vessel which is closed by a septum and which is connected by a gas line to a gas vial. In this procedure, the substances are again transferred gently into the appliance, but an additional gas reservoir is required.

In all three procedures, care must be taken to ensure that, when inserting the needle into the pressurized injector of the chromatograph, gas flows back through the filter into the syringe or into the gas delivery system, since otherwise there is a danger of the substances being desorbed in the wrong direction.

This would lead to incorrect results and to so-called carry-over effects, i.e. carry-over of substances from one measurement to the next. This effect can generally be avoided by the pressure in the gas chromatograph being cut off during the injection. This is also advisable since in this way the substances can be transported in the smallest possible amount of gas from the filter into the chromatograph, and the gas in which the substances are transported into the chromatograph is not diluted by the regular gas flow in the chromatograph. The smaller the amount of desorption gas, the sharper the signals and, accordingly, the higher the sensitivity of the equipment.